Supporting Information For:

High Field Solid-State NMR Spectroscopy Investigation of ^{15}N-Labeled Rosette Nanotubes: Hydrogen Bond Network and Channel-Bound Water

Hicham Fenniri,[#,‡,†,*] Grigory A. Tikhomirov,[‡,†] Darren H. Brouwer,[§] Souhaila Bouatra,[‡,†] Mounir El Bakkari,[‡,†] Zhimin Yan,[†] Jae-Young Cho,[†] Takeshi Yamazaki[†]

[#]*313 Snell Engineering Center, 360 Huntington Avenue, Northeastern University, Boston, MA 02115, USA.*

[‡]*Department of Chemistry and* [†]*National Institute for Nanotechnology (NINT-NRC), University of Alberta, 11421 Saskatchewan Drive, Edmonton, Alberta T6G 2M9, Canada.*

[§]*Department of Chemistry, Redeemer University College, 777 Garner Road East, Ancaster, Ontario L9K 1J4, Canada.*

*Corresponding Author:

Professor Hicham Fenniri

Tel: (617) 373-7690

Email: h.fenniri@neu.edu

Abbreviations

ACN (acetonitrile); anh (anhydrous); app (apparent); aq (aqueous); Bn (benzyl); Boc (*tert*–butyloxycarbonyl); br (broad); $CHCl_3$ (chloroform); conc (concentrated); DIEA (diisopropylethylamine); d (doublet); DCE (dichloroethane); DCM (dichloromethane); dH_2O (deionized NanoPure water); DMAP (4–N,N-dimethylaminopyridine); DMF (N,N–dimethylformamide); DMSO (dimethylsulfoxide); EA (ethylacetate); ESI–MS (electrospray ionization mass spectrometry); Et_2O (diethylether), h (hour); HCl (hydrochloric acid); m (multiplet); MeOH (methanol); min (minute); mp (melting point); NMR (nuclear magnetic resonance); q (quartet); rbf (round-bottom flask), R_f (retention factor); rt (room temperature); s (singlet); sat (saturated); SEM (scanning electron microscopy); t (triplet); *t*–Bu (*tert*–butyl); TEA (triethylamine); TEM (transmission electron microscopy); TFAA (trifluoroacetic anhydride); THF (tetrahydrofuran); TLC (thin layer chromatography).

General

All the reagents and solvents are commercially available from Aldrich, Novabiochem, BaChem, Fluka, or Fisher Scientific, and were used without further purification. ^{15}N-labeled **1** was synthesized as shown in Figure S1. Reagent grade ACN, DCM and THF were purified on an MBraun solvent purification system. For column chromatography, commercial solvents were used without purification. Chromatographic supports were silica flash Merck 60 (0.040–0.063 mm) or silica gel Merck 60 (0.063–0.2 mm) for gravity chromatography. Silica–coated TLC plates (Merck F 60254) were used for monitoring reaction progress.

Solution state ^{1}H, ^{13}C and ^{15}N–NMR spectra were recorded on Varian Inova NMR spectrometers (400, 500, 600, or 900 MHz) with the solvent as internal reference. The NMR data is presented as follows: chemical shift, peak assignment, multiplicity, coupling constant, integration.

Assignments were made using 2D–NMR techniques (COSY, TROESY, HMBC, HMQC). The mass spectra were performed at the Mass Spectrometry Laboratory at the Department of Chemistry, University of Alberta, or in the Analytical Laboratory of The National Institute for Nanotechnology, University of Alberta.

Synthesis of ^{15}N-labelled and non-labeled G∧C bases:

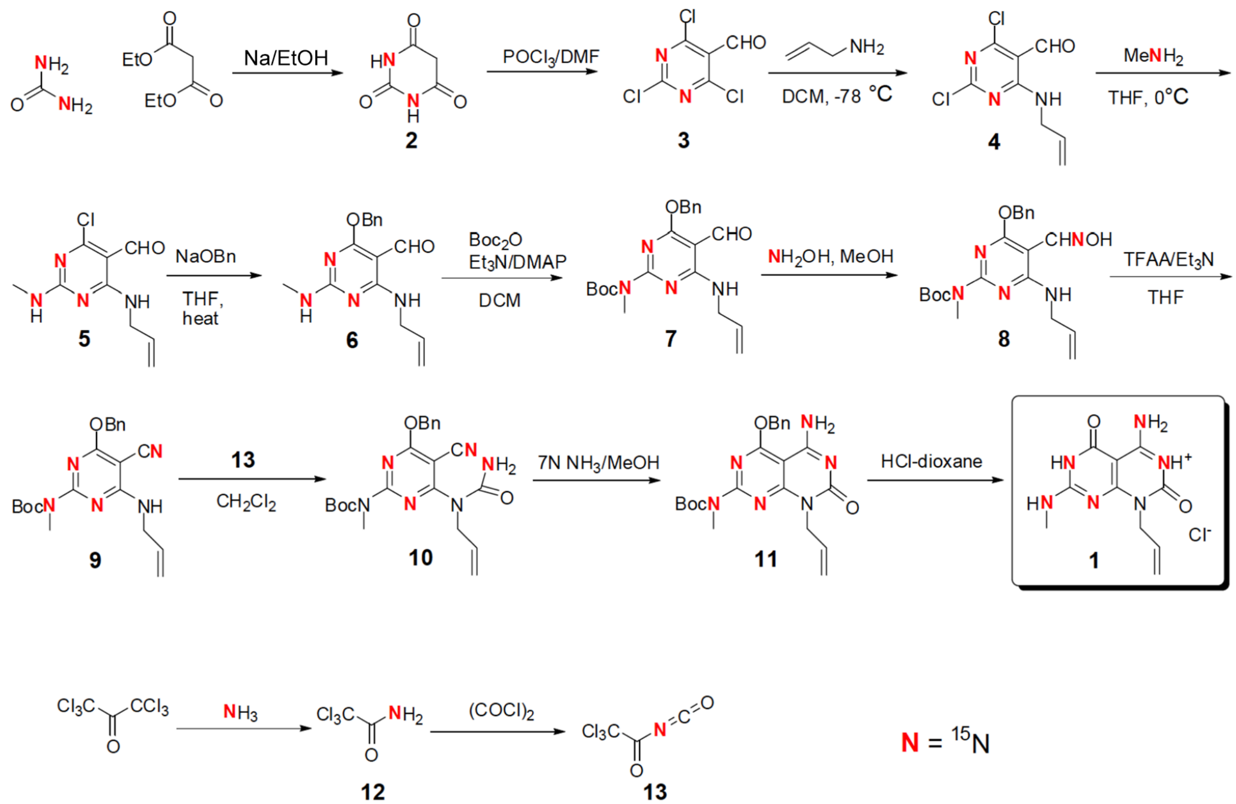
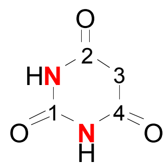


Figure S1. Synthesis of compound **1**.

Synthesis of compound **2**



To a round-bottom flask (rbf) fitted with a reflux condenser and calcium chloride drying tube was added EtOH (anh, 63 mL) and sodium metal (1.15 g, 0.05 mol). The suspension was stirred at rt until dissolution, after which was added ethyl malonate (8.00 g, 0.05 mol) followed by urea (3.20 g, 0.05 mol) in hot (70°C) EtOH (anh, 12.5 mL). The mixture was heated to reflux for 7 h, after which a white solid separated rapidly. A warm solution of dH_2O (50 mL, 50°C) and HCl (conc., enough to lower the pH to <5) were added. The white precipitate was collected by vacuum filtration, washed with cold dH_2O (10 mL), and dried in an oven at 105-110°C for 4 h to yield pure barbituric acid **2** (4.60 g, 68%). mp: 243°C.

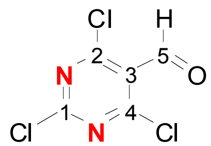
^{1}H-NMR (400 MHz, DMSO) δ (ppm): 3.45 (C_3H, s, 2H), -0.91 (N, d, $J_{N\text{-}H}$ = 92.4 Hz, 2H).

^{13}C-NMR (100 MHz, DMSO) δ (ppm): 167.69 (C_2, C_4), 151.59 (C_1), 39.48 (C_3).

^{15}N-NMR (40 MHz, DMSO) δ (ppm): 154.37 (s).

High-resolution EI-MS: Calculated for $C_4H_4{}^{15}N_2O_3^+$ (M^+)/z 130.0157. Observed: *m/z* 130.0163.

Synthesis of compound **3**



Barbituric acid **2** (7.80 g, 60 mMol) was added to a stirred solution of $POCl_3$ (36 mL, 59.8 g, 389 mMol) and DMF (4.61 mL, 4.38 g, 60 mMol) at rt under N_2 atmosphere. The mixture was heated to reflux for 15 h, then allowed to cool to rt. Excess $POCl_3$ was evaporated (rotavap), and the resulting viscous oil was carefully poured over crushed ice (150 g) while being vigorously stirred. The resulting precipitate was collected by vacuum filtration and dried in vacuum to yield the desired compound **3** ($C_5HCl_3{}^{15}N_2O$, 10.02 g, 78%) as yellow crystalline solid. R_f = 0.43 (10% EA/Hex). mp = 130ºC.

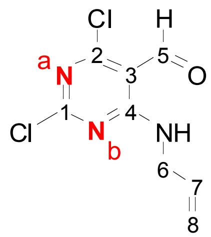
^{1}H-NMR (400MHz, $CDCl_3$) δ (ppm): 10.42 (C_5H, s, 1H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm): 184.60 (C_5), 164.07 (C_1), 123.03 (C_2, C_4).

^{15}N-NMR (50 MHz, $CDCl_3$) δ (ppm): 288.91 (s).

High-resolution EI-MS: Calculated for $C_5Cl_3{}^{15}N_2O^+$ $(M–H)^+$/z 210.9011. Observed: *m/z* 210.9012.

Synthesis of compound **4**



To a stirred solution of **3** (4.52 g, 21.2 mMol) in DCM (anh, 40 mL) at -78ºC under N_2 atmosphere was slowly added allylamine (3.2 mL, 2.42 g, 42.4 mMol). The resulting mixture was stirred at -78ºC for 6 h. The reaction was quenched with dH_2O (20 mL) and extracted with DCM (180 mL). The organic layer was washed with H_2O (2×40 mL) and brine (100 mL), dried over Na_2SO_4 (anh), filtered and evaporated (rotavap). Purification via column chromatography (0-2% EA/Hex) yielded compound **4** as colorless liquid ($C_8H_7Cl_2N^{15}N_2O$, 3.63 g, 73%). R_f = 0.33 (10% EA/Hex).

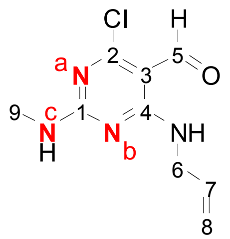
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 10.30 (C_5H, s, 1H), 9.36 (NHC_6, broad (br), s, 1H), 5.94-5.85 (C_7H, m, 1H), 5.27-5.20 (C_8H, m, 2H), 4.21 (C_6H, m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 190.40 (C_5), 165.94, 162.70 ($C_{1,}$ C_2), 161.5 (C_4), 132.11 (C_7), 117.53 (C_8), 106.62 (C_3), 43.46 (C_6).

^{15}N-NMR (40 MHz, $CDCl_3$) δ (ppm): 256.01 (^{15}N*a*, d, ^{2}J= 1.8 Hz), 245.22 (^{15}N*b*, d, ^{2}J= 1.8 Hz).

High-resolution EI-MS: Calculated for $C_8H_7Cl_2{}^{15}N_2{}^{14}NO^+$ (M^+)/z 233.9980. Observed: *m/z* 233.9980.

Synthesis of compound **5**



To a stirred solution of **4** (3.00 g, 12.81 mMol) and methylamine hydrochloride (0.966 g, 14.09 mMol) in THF (40 mL) at -78ºC under N_2 atmosphere was added TEA (5.4 mL, 38.4 mMol). The resulting mixture was stirred at -78ºC for 3 h, after which it was allowed to warm to rt and stirred for 18 h. The reaction mixture was quenched with NH_4Cl (saturated aq., 10 mL) and the THF was evaporated (rotavap). The residual solid was dissolved in EA (150 mL), washed with dH_2O (10 mL) and brine (5 mL), dried over Na_2SO_4 (anh), filtered, and evaporated (rotavap). Purification via column chromatography (10% EA/Hex) yielded the desired product **5** ($C_9H_{11}ClN^{15}N_3O$, 2.57 g, 87%) as a white crystalline solid. R_f = 0.22 (10% EA/Hex). mp = 156ºC.

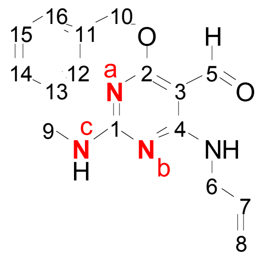
^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 10.05 (C_5H, s, 1H), 9.38 (NHC_6, br, s, 1H), 6.81 (HN*c*, d, $J_{N\text{-}H}$ = 93.2 Hz, 1H), 5.94-5.90 (C_7H, m, 1H), 5.27-5.15 (C_8H, m, 2H), 4.18 (C_6H, m, 2H), 3.01 (C_9, d, ^3J = 4.4 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 188.81 (C_5), 165.15, 162.11 ($C_{1,}$ C_2), 161.9 (C_4), 133.53 (C_7), 116.39 (C_8), 101.48 (C_3), 42.87 (C_6), 28.17 (C_9).

^{15}N-NMR (40 MHz, $CDCl_3$) δ (ppm): 226.50 (N*b*, dd, $^2J_1$ = 7.9 Hz, $^2J_2$ = 6.8 Hz), 194.83 (N*a*, dd, $^2J_1$ = 7.9 Hz, $^2J_2$ = 6.1 Hz), 90.96 (N*c*, dd, $^2J_1$ = 6.8 Hz, $^2J_2$ = 6.1 Hz).

High-resolution ESI-MS: Calculated for $C_9H_{12}Cl^{15}N_3{}^{14}NO^+$ (M+H$^+$)/z 230.0605. Observed: *m/z* 230.0607.

Synthesis of compound **6**



To a stirred suspension of NaH (0.183 g, 7.01 mMol) in THF (anh, 10 mL) at rt under N_2 atmosphere was added benzyl alcohol (0.67 g, 0.64 mL, 6.1 mMol). The reaction mixture was stirred at rt for 15 min, after which the solution was cooled to 0ºC and a solution of compound **5** (0.7 g, 3.05 mMol) in THF (anh, 20 mL) was added. The mixture was allowed to warm to rt then heated to reflux for 22 h. The crude reaction mixture was cooled to 0ºC, carefully quenched with aq NH_4Cl (sat, 5 mL) and the solvent was evaporated (rotavap). The residual solid was dissolved in Et_2O (100 mL), washed with dH_2O (100 mL) and brine (50 mL), dried over Na_2SO_4 (anh), filtered, and evaporated (rotavap). Purification via column chromatography (0 to 5% EA/Hex) yielded **6** ($C_{16}H_{18}N^{15}N_3O_2$, 0.75 g, 82%) as a white solid. R_f = 0.51 (30% EA/Hex). mp = 56ºC.

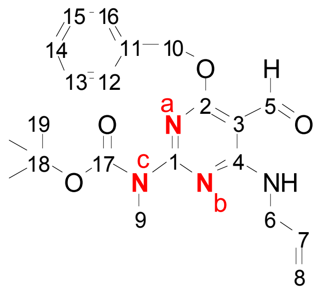
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 10.01 (C_5H, s, 1H), 9.36 (NHC_6, br, s, 1H), 7.39-7.32 (C_{12}H-C_{16}H, m, 5H), 5.94-5.93 (C_7H, br, m, 1H), 5.49-5.13 (C_8H, C_{10}H, m, 4H), 4.19 (C_6H, br, s, 2H), 3.01 (C_9, s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm): 185.88 (C_5), 171.26 (C_4), 163.32, 163.29 (C_1, C_2), 136.60 (C_{11}), 134.34 (C_7), 128.38, 127.77, 126.82 (C_{12}-C_{16}), 115.81 (C_8), 92.72 (C_3), 67.37 (C_{10}), 42.53 (C_6), 28.09 (C_9).

^{15}N-NMR (40 MHz, $CDCl_3$) δ (ppm): 195.57 (N*b*, br, d, ^2J = 6.6 Hz), 188.31 (N*a*, br, d, ^2J = 6.6 Hz), 87.91 (N*c*, m).

High-resolution ESI-MS: Calculated for $C_{16}H_{19}{}^{15}N_3{}^{14}NO_2^+$ (M+H$^+$)/z 302.1414. Observed: *m/z* 302.1420.

Synthesis of compound **7**



To a stirred solution of compound **6** (1.16 g, 3.80 mMol) and 4-N,N-dimethylaminopyridine (0.235 g, 1.9 mMol) in THF (anh, 20 mL) at rt under N_2 atmosphere was added TEA (1.16 g, 1.61 mL, 11.5 mMol). Boc_2O (1.26 g, 5.77 mMol) was then added and the mixture was stirred at rt for 18 h. The reaction mixture was quenched with dH_2O (5 mL) and the THF was evaporated (rotavap). The residual solid was dissolved in EA (100 mL), washed with 10% aq. citric acid (10 mL), dH_2O (2×10 mL), 5% aq. $NaHCO_3$ (10 mL), and brine (10 mL), dried over Na_2SO_4 (anh), filtered, and evaporated (rotavap) to yield compound **7** ($C_{21}H_{26}N^{15}N_3O_4$, 1.27 g, 83%) as a white crystalline solid. R_f = 0.38 (10% EA/Hex). mp = 54ºC.

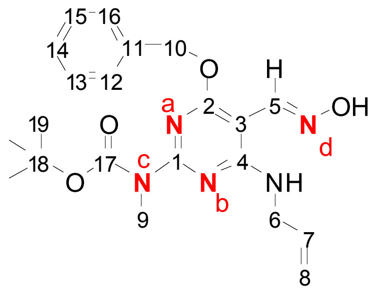
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 10.14 (C_5H, s, 1H), 9.22 (NHC_6, br, t, 1H), 7.42-7.35 (C_{12}H-C_{16}H, m, 5H), 5.93-5.91 (C_7H, m, 1H), 5.48 (C_{10}H, s, 2H), 5.25-5.13 (C_8H, m, 2H), 4.18 (C_6H, m , 2H), 3.38 (C_9H, s, 3H), 1.55 (C_{19}, s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 187.65 (C_5), 171,48 (C_4), 162.74, 162.68 ($C_{1,}$ C_2), 153.90 (C_{17}), 136.32 (C_{11}), 134.08 (C_7), 128.54, 128.20, 128.05 (C_{12}-C_{16}), 116.23 (C_8), 94.29 (C_3), 81.92 (C_{18}), 68.24 (C_{10}), 43.02 (C_6), 34.99 (C_9), 28.21 (C_{19}).

^{15}N-NMR (40 MHz, $CDCl_3$) δ (ppm): 212.21 (N*b*, dd, $^2J_1$ = $^2J_2$ = 5.6 Hz d), 209.54 (N*a*, dd, $^2J_2$ = 5.6 Hz, $^2J_3$ = 5.0 Hz), 120.80 (N*c*, dd, $^2J_1$ = 5.6 Hz, $^2J_3$ = 5.0 Hz).

High-resolution ESI-MS: Calculated for $C_{21}H_{26}{}^{15}N_3{}^{14}NO_4Na^+$ (M+Na$^+$)/z 424.1757. Observed: *m/z* 424.1760.

Synthesis of compound **8**



To a stirred solution of **7** (1.42 g, 3.5 mMol) in pyridine (17 mL) at rt under N_2 atmosphere was added hydroxylamine hydrochloride (0.491 g, 6.97 mMol). The mixture was heated to reflux for 3 h, cooled to rt and quenched with dH_2O (10 mL). The solvent was evaporated (rotavap) and the residual solid was dissolved in EA (100 mL), washed with dH_2O (20 mL) and brine (10 mL), dried over Na_2SO_4 (anh), filtered, and evaporated (rotavap) to yield compound **8** ($C_{21}H_{27}N^{15}N_4O_4$, 1.60 g, 100%). R_f = 0.50 (30%EA/Hex).

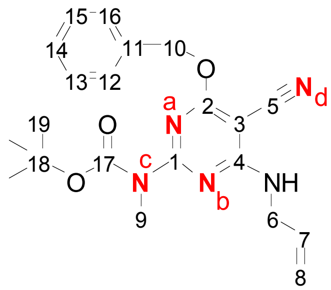
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 8.48 (C_5H, d, ^4J = 1.8 Hz, 1H), 8.05 (NHC_6, t, ^3J = 6.5 Hz, 1H), 7.60 (NOH, br, s, 1H), 7.41-7.28 (C_{12}H-C_{16}H, m, 5H), 5.99-5.89 (C_7H, m, 1H), 5.44 (C_{10}H, s, 2H), 5.28-5.10 (C_8H, m, 2H), 4.25-4.18 (C_6H, m, 2H), 3.41 (C_9H, s, 3H), 1.56 (C_{19}, s, 9H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm): 166.88 (C_4), 160.16, 158.96 (C_1, C_2), 154.03 (C_{17}), 145.42(C_5), 136.74 (C_{11}), 134.76 (C_7), 128.33, 127.95 (C_{12}-C_{16}), 115.37 (C_8), 88.05 (C_3), 81.16 (C_{18}), 67.94 (C_{10}), 43.24 (C_6), 34.70 (C_9), 28.23 (C_{19}).

^{15}N-NMR (50 MHz, $CDCl_3$) δ (ppm): 348.01 (N*d*, s), 217.52 (N*b*, dd, $^2J_1$ = $^2J_2$ = 5.4 Hz), 212.91 (N*a*, dd, $^2J_2$ = 5.4 Hz, $^2J_3$ = 5.0 Hz), 79.43 (N*c*, d, $^2J_1$ = 5.4 Hz, $^2J_3$ = 5.0 Hz).

High-resolution ESI-MS: Calculated for $C_{21}H_{26}{}^{15}N_4{}^{14}NO_4^+$ ($M+H^+$)/z 418.2017. Observed: *m/z* 418.2017.

Synthesis of compound **9**



To a solution of compound **8** (1.44 g, 3.45 mMol) and TEA (1.44 mL, 1.04 g, 10.35 mMol) in anh THF (35 mL) at 0ºC under N_2 atmosphere was added TFAA (0.72 mL, 1.08 g, 5.17 mMol). After stirring for 15 min, the mixture was allowed to warm to rt before it was heated to reflux for 5 h. The reaction mixture was cooled to rt, quenched with dH_2O (10 mL) and the solvent was evaporated (rotavap). The residual solid was dissolved in EA (150 mL), washed with dH_2O (2×30 mL), 10% aq citric acid (15 mL), dH_2O (30 mL), 5% aq $NaHCO_3$ (30 mL), and brine (30 mL), dried over Na_2SO_4 (anh), filtered, and evaporated (rotavap). Purification via column chromatography (3% EA/Hex) yielded compound **9** ($C_{21}H_{25}N^{15}N_4O_3$, 1.13 g, 82%) as a white solid. R_f = 0.64 (30% EA/Hex). mp = 68ºC.

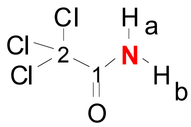
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44-7.31 (C_{12}H-C_{16}H, m, 5H), 5.92-5.86 (C_7H, m, 1H), 5.46 (C_{10}H, s, 2H), 5.24 (C_8H, d, ^3J = 17.2, 1H), 5.18 (C_8H, d, ^3J = 10.4, 1H), 4.16 (C_6H, t, ^3J = 5.6 Hz, 2H), 3.35 (C_9H, s, 3H), 1.54 (C_{19}, s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 170.21 (C_4), 163.89, 162.30 (C_1, C_2), 153.52 (C_{17}), 135.82 (C_{11}), 133.60 (C_7), 128.39, 128.08, 127.89 (C_{12}-C_{16}), 117.06 (C_8), 114.70 (C_5), 81.97 (C_{18}), 68.52 (C_{10}), 43.57 (C_6), 34.49 (C_9), 28.10 (C_{19}).

^{15}N-NMR (40 MHz, $CDCl_3$) δ (ppm): 274.65 (N*d*, s), 211.48 (N*a*, dd, $^2J_1$ = 6.0 Hz, $^2J_2$ = 1.4 Hz), 211.17 (N*b*, dd, $^2J_2$ = 6.0 Hz, $^2J_3$ = 1.4 Hz), 119.56 (N*c*, t, $^2J_1$ = $^2J_3$ = 6.0 Hz).

High Resolution ESI-MS: Calculated for $C_{21}H_{25}{}^{15}N_4{}^{14}NO_3Na^+$ $(M+Na^+)/z$ 422.1731. Observed: *m/z* 422.1744.

Synthesis of compound **12**



Hexachloroacetone (35.3 g, 22.4 mL, 0.13 mol) in $CHCl_3$ (75 mL) was cooled to -78ºC under N_2 atmosphere. $^{15}NH_3$ gas was then added with stirring over 3 h while the reaction mixture was maintained at -80ºC or less. The mixture was then allowed warm to -10ºC for 1h. The solid was collected by vacuum filtration and dried at rt under vacuum to yield compound **12** as a white solid ($C_2H_2Cl_3{}^{15}NO$, 19.02 g, 95%). mp = 142ºC.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54 (H_a or H_b, d, J = 90.0 Hz, 1H). 7.27 (H_b or H_a, d, J = 90.0 Hz, 1H)

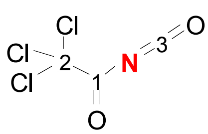
^{13}C-NMR (125 MHz, DMSO-d_6) δ (ppm): 162.95 (C_1), 93.11(C_2).

^{15}N-NMR (50 MHz, DMSO-d_6) δ (ppm): 102.02 (s).

ESI-MS Calculated for H_2CNO^+ $(M-CCl_3)^+/z$, 44. Observed, *m/z*, 44(100%).

FTIR (KBr, rt), (cm^{-1}): 3364-3177 (NH_2), 1688 (C=O), 1611 (C-N), 750-850 (C-Cl).

Synthesis of compound **13**



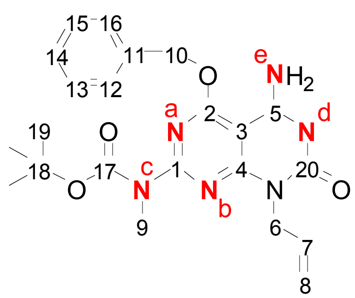
To a three neck 250 mL rbf fitted with a magnetic stirrer, a thermometer, and a condenser carrying a calcium chloride tube was added compound **12** (10.0 g, 0.06 mol) and 1.2-DCE (anh, 40 mL). The mixture was cooled to 0°C and oxalyl chloride (7.76 g, 5.18 mL, 0.6 mol) was added. The reaction mixture was removed from the ice bath, stirred for 1h, and then heated to reflux for 24 h. The solvent was evaporated at 83°C under atmosphere pressure. Purification via vacuum distillation at 50-55°C (at 130 mm Hg) yielded **13** (4.4 g, 60%, bp = 80-85°C at 20 mm) as a colorless liquid.

^{13}C-NMR (125 MHz, CD_3CN) δ (ppm): 159.79 (C_1), 131.38 (C_3), 92.28 (C_2).

^{15}N-NMR (50 MHz, DMSO-d_6) δ (ppm): 246.79 (s)

Infrared IR (KBr, rt), γ (cm^{-1}): 2243 (N=C=O), 1758 (C=O).

Synthesis of compound **11**



To a solution of compound **10** (0.95 g, 2.38 mMol) in DCM (18 mL) at 0°C under N_2 atmosphere was added trichloroacetyl isocyanate **13** (2.7 g, 1.71 mL, 14.3 mMol) dropwise over a period of 15 min. After stirring for 2 h at 0°C, the mixture was allowed to warm to rt and was stirred for 18 h. To the crude reaction mixture at rt under N_2 atmosphere was added NH_3 (7 M in MeOH, 60 mL) and the mixture was stirred for 3 h. The solvents were evaporated (rotavap). Purification via column chromatography (30-100% Hex/EA) yielded the desired compound **11** as white solid ($C_{22}H_{26}N^{15}N_5O_4$, 0.53 g, 50%). R_f = 0.26 (50% Hex/EA). mp =192°C.

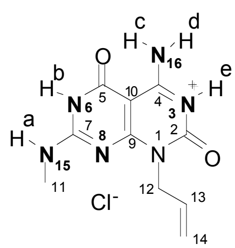
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47-7.39 (C_{12}H-C_{16}H, m, 5H), 6.95 (HN_e, dd, ^{1}J = 93 Hz, ^{2}J = 6.79 Hz, 1H), 6.25-6.46 (HN_e, br, m, 1H), 6.00-5.91 (C_7H, m, 1H), 5.60 (C_{10}H, s, 2H), 5.24 (C_8H, m, 2H), 4.16 (C_6H, m, 2H), 3.45 (C_9H, s, 3H), 1.59 (C_{19}, s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 166.51 (C_4), 161.06, 161.00, ($C_{1,}$ C_2), 160.52 (C_5), 155.69 (C_{17}), 153.31 (C_{20}), 153.08 (C_{21}, C_{24}), 135.10 (C_{11}),132.61 (C_7), 129.19, 128.80, (C_{12}-C_{16}), 117.66 (C_8), 86.16 (C_3), 82.81 (C_{22}, C_{25}), 77.59 (C_{18}), 70,32 (C_{10}), 44.91 (C_6), 35.17(C_9), 28.51 (C_{19}).

^{15}N-NMR (40 MHz, $CDCl_3$) δ (ppm): 218.95 (N_b, dd, ^{2}J= 5.6 Hz, ^{2}J= 1.2 Hz), 216.83 (N_a, dd, ^{2}J = 5.6 Hz, ^{2}J= 1.2 Hz), 200.61 (N_e, d, ^{2}J= 5.8 Hz), 120.74 (N_d, d, ^{2}J = 5.8 Hz), 120.74 (N_c, dd, $^2J_1$ = $^2J_2$ = 6.0 Hz).

High-resolution ESI-MS: Calculated for $C_{22}H_{26}{}^{15}N_5{}^{14}NO_4Na^+$ (M+Na^+)/z 466.1759. Observed: *m/z* 466.1801.

Synthesis of compound **1·H**$^+$



Compound **11** (0.044 g, 0.1 mMol) was dissolved in 4M solution of HCl in dioxane (4 mL) and the mixture was heated to reflux for 2 h. The white precipitate was collected by vacuum filtration and washed with DCM (5×10 mL) to yield compound **1·H**$^+$ as a white solid (0.028 g, 100%).

HRMS (ESI) calcd for $C_{10}H_{13}{}^{15}N_5{}^{14}NO_4$ (M+H^+) *m/z* 254.0977, found *m/z* 254.0978.

NMR data for compound **1** is summarized in Table S1. Selected spectra follow the table.

Table S1. Chemical shifts and correlations for two tautomers based on ^{1}H, ^{13}C, ^{15}N NMR, ^{1}H-^{13}C HMQC,[a] ^{1}H-^{13}C HMBC,[b] ^{1}H-^{15}N HSQC,[c] ^{1}H-^{15}N HMQC,[d] ^{1}H-^{15}N gHMBC,[e] and NOESY.[f]

Carbon/ Nitrogen	δ (ppm)	Correlation to Proton[a-e]	Proton	δ (ppm)	NOE to Proton[f]
C(2)	147.99	**12[b], 13[b], 14[b], c[b]**	H(b)	12.07	**a**
C(4)	156.51	**c[b], d[b]**	H(c)	9.20	**d, e**
N(16)	99.08	**c[c], d[c], c[d], d[d], c[e], d[e]**	H(d)	8.71	**c, e**
C(5)	161.33	**c[b]**			
N(8)	180.65	**a[d], *a*[e]**			
C(7)	155.92	**a[b], 11[b]**			
N(15)	92.24	**a[c], a[d], 11[d], e[d], 11[e], a[e]**	H(a)	8.35	**11, b**
C(11)	28.00	**a, 11[a]**	H(11)	2.92	**a, b, 12**
N(6)	148.32	**b[c], b[d], b[e], a[e]**	H(e)	12.50	**c, d**
C(9)	160.00	**12[b],13[b],14[b], a[b], d[b]**			
C(10)	83.01	**b[b], c[b], d[b], e[b]**			
C(12)	44.72	**13[b], 14[b], 12[a]**	H(12)	4.63	**11, 13, 14**
C(13)	132.36	**12[b], 14[b], 13[a]**	H(13)	5.78	**12, 14**
C(14)	118.18	**12[b], 13[b], 14[a]**	H(14)	5.14	**12, 13**
N(3)	137.31	**e[c], e[d]**			

([a]) ^{13}C HMQC, ([b]) ^{1}H-^{13}C HMBC, ([c]) ^{1}H-^{15}N HSQC, ([d]) ^{1}H-^{15}N HMQC, ([e]) ^{1}H-^{15}N gHMBC, and ([f]) NOESY. The spectra were recorded in the solvents and at temperatures where optimal resolution is obtained. ^{1}H, ^{1}H-^{13}C HMQC, ^{1}H-^{13}C HMBC, ^{1}H-^{15}N HSQC, ^{1}H-^{15}N HMQC, ^{1}H-^{15}N gHMBC, and NOESY were recorded in 1:1 (v/v) $CDCl_3$-DMSO-d_6 at -40°C. ^{13}C, ^{15}N NMR were recorded in DMSO-d_6 at 27°C. NOESY was recorded in DMF-d_7 at -60°C.

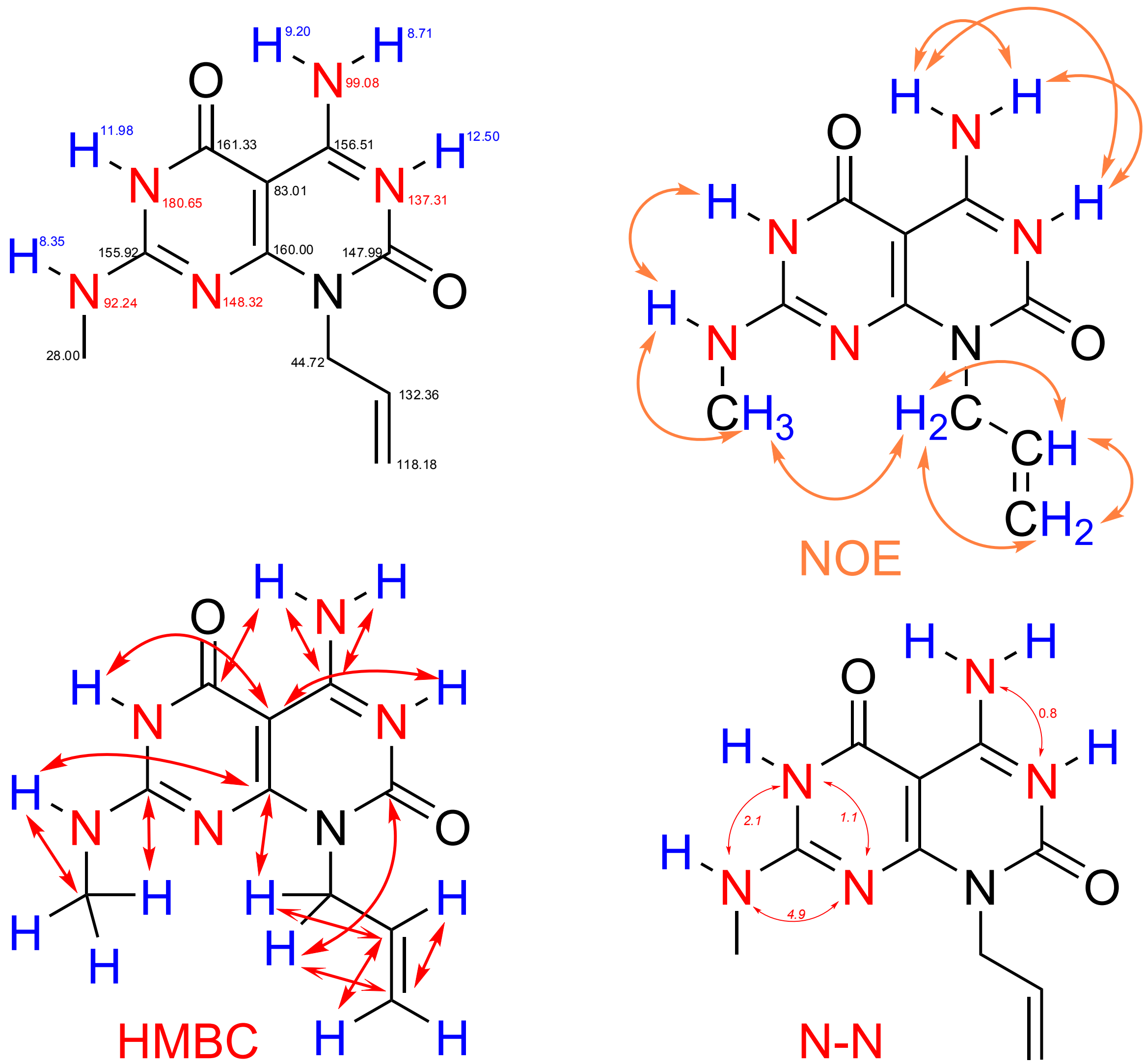


Figure S2. H, C, N resonances assignments and major correlations in NOE, HMBC, and ^{15}N NMR spectra in solution. N-N J-couplings are in Hz.

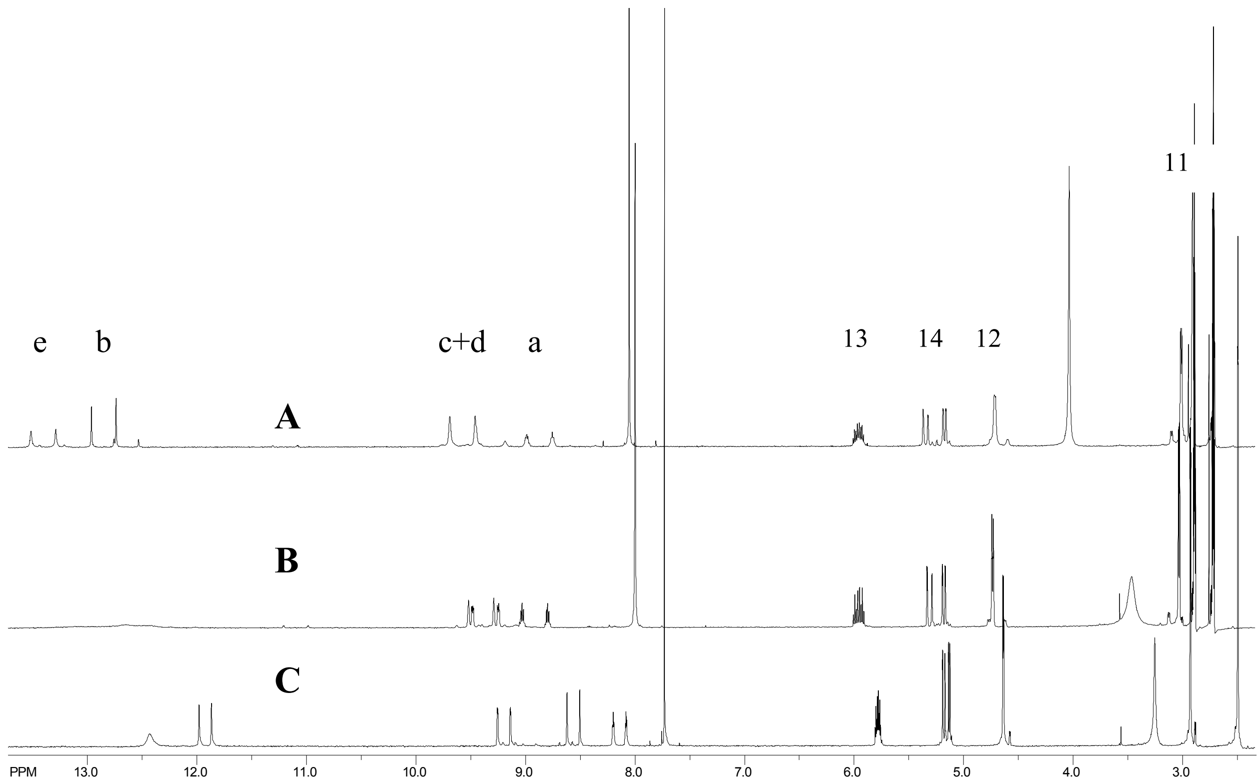


Figure S3. ^{1}H NMR spectra of **1**$\cdot$H$^+$ in (A) DMF-d_7 (-50°C, 500 MHz), (B) DMF-d_7, 27°C, 500 MHz, (C) $CDCl_3$–DMSO-d_6 (1:1/v:v), 5°C, 800 MHz. The assignments are given in Table S1. Note sharpening of the NH signals as polarity of the solvent and temperature decrease. Note that signals of protons c and d overlap at -60°C and are resolved at +27°C.

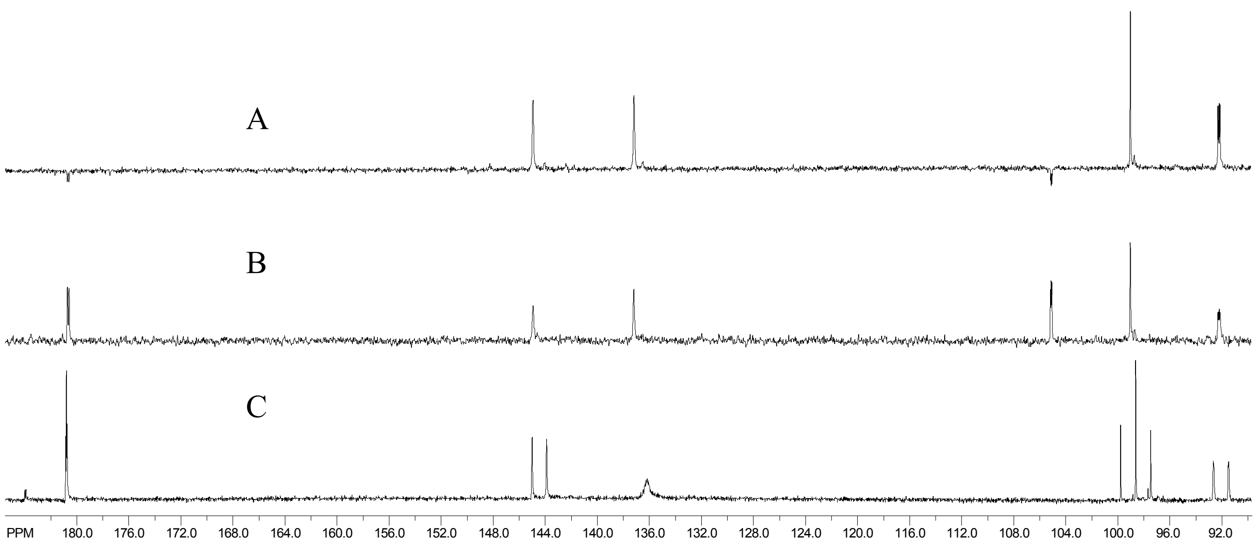


Figure S4. ^{15}N NMR spectra of **1**$\cdot H^+$ in (A) DMF-d_7 (27°C, 400 MHz, 10 h), with NOEs) and (B) DMF-d_7 (27°C, 500 MHz, 10 h) without NOEs, (C) $CDCl_3$-DMSO-d_6 (1/1 v/v) coupled to H. Signal at 105 ppm in (A, B) is DMF.

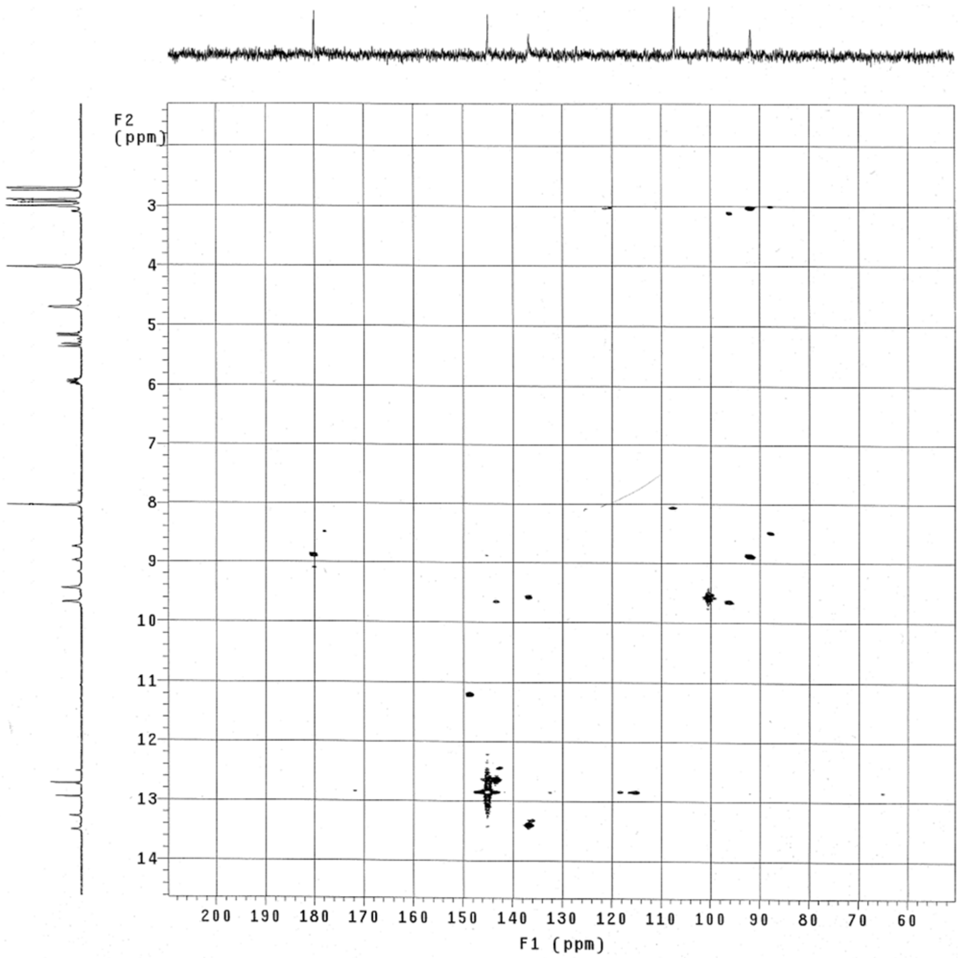


Figure S5. ^{1}H-^{15}N HMQC spectrum of **1**·H$^+$ in DMF-d$_7$ (-60°C, 400 MHz) J_{xh} = 10 Hz.

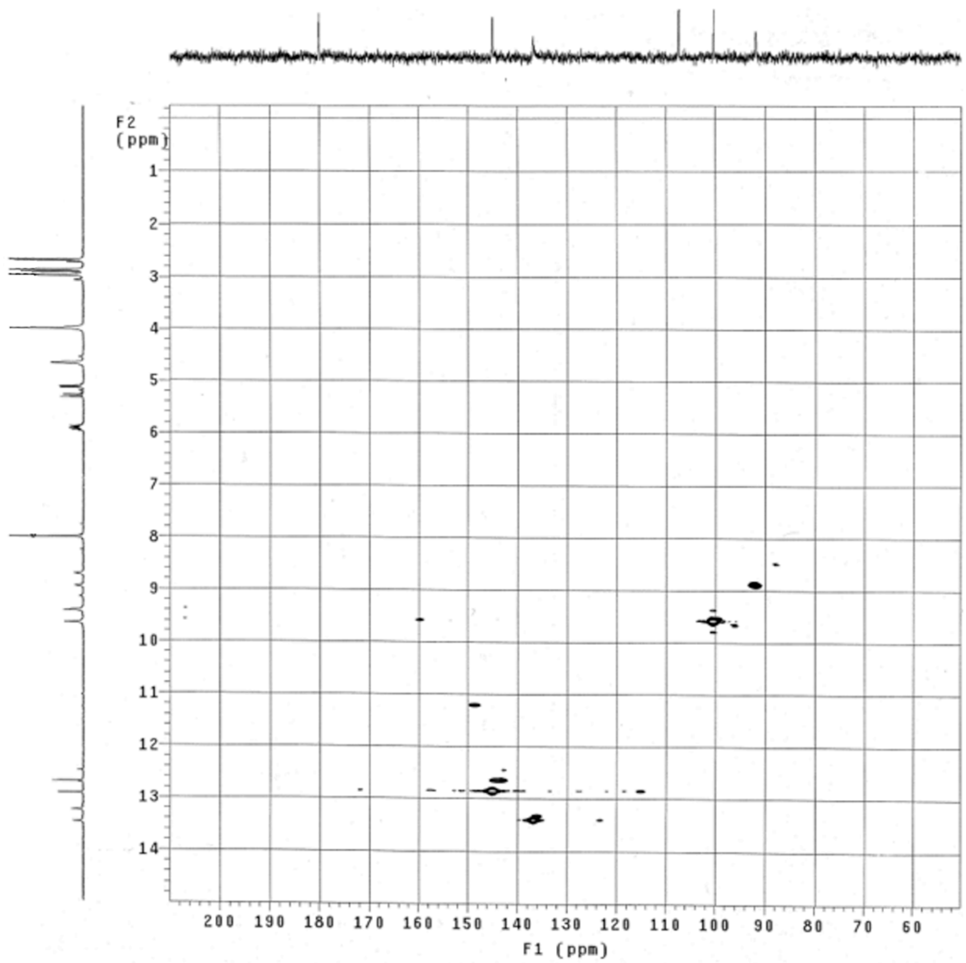


Figure S6. ^{1}H-^{15}N HMQC spectrum of **1**$\cdot H^{+}$ in DMF-d_7 (-60°C, 400 MHz) J_{1xh} = 90 Hz.

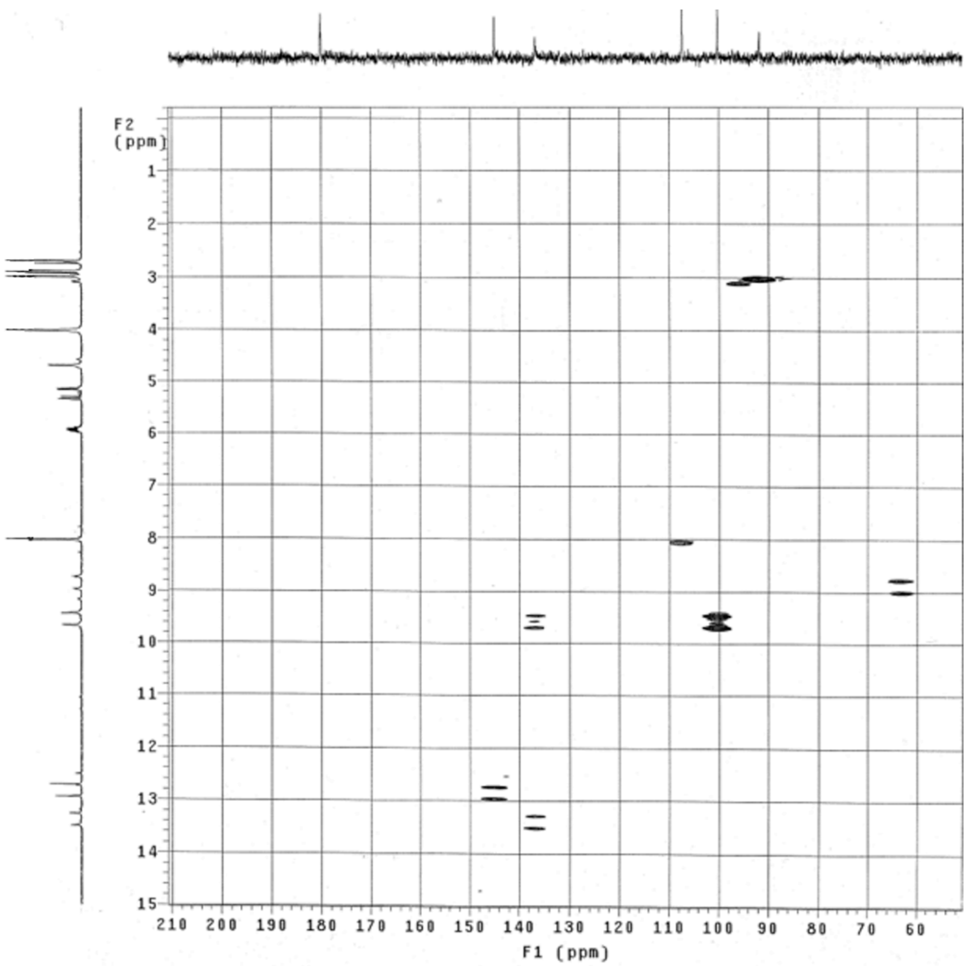
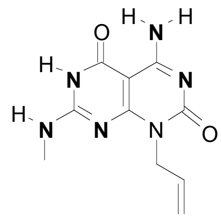


Figure S7. ^{1}H-^{15}N HMBC spectrum of **1**·H^{+} in DMF-d_7 (-60°C, 400 MHz) J_1 = 90 Hz, J_n = 10 Hz.

Synthesis of compound **1**



Compound **1·H$^+$** (40 mg, 0.141 mmol) was dissolved in MeOH (200 mL, HPLC grade) and NH_3 (5 mL, 7 M in MeOH) was added. Immediate precipitation occurred. Solvent and excess ammonia were evaporated (rotavap), the precipitate was washed with dH_2O (5×20 mL), and dried in vacuum for 12 h to yield **1** (35 mg, 0.141 mmol, 100%) as a white solid.

HRMS (ESI) calcd for $C_{10}H_{13}{}^{15}N_5{}^{14}NO_4$ (M+H$^+$) *m/z* 254.0977, found *m/z* 254.0975.

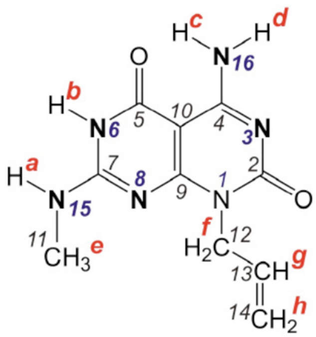
Solid-State NMR

Ultrahigh-field solid-state ^{1}H MAS NMR and two-dimensional ^{1}H-^{1}H and ^{1}H-^{15}N correlation experiments were carried out on a Bruker AVANCE-II 900 instrument with a 21.1 T magnetic field strength and operating at 900.08 and 91.20 MHz Larmor frequencies for ^{1}H and ^{15}N, respectively. The experiments were performed with a 1.3 mm double resonance CP-MAS probe enabling a MAS frequency of 60 kHz. The ^{1}H MAS NMR spectra were obtained with 16 scans and a recycle delay of 5 s. The ^{1}H-^{1}H 2D DQ correlation experiments employed one rotor period (16.67 μs) of back-to-back (BABA)[1] DQ excitation and reconversion. The ^{1}H 90° pulse length was 1.5 μs. The sweep width in the DQ dimension was 30 kHz and the States method[2] was used for quadrature detection in the indirect dimension. Two experiments, each with 16 scans, were acquired at each of the 40 t_1 increments. The 2D ^{1}H-^{15}N CP-HETCOR experiments employed 1 ms of ^{1}H to ^{15}N cross-polarization with ^{1}H and ^{15}N nutation frequencies of 40 and 100 kHz, respectively. Weak ^{1}H cw decoupling with a ^{1}H nutation frequency of 10 kHz was applied during the acquisition period. The sweep width in the indirect ^{1}H dimension was 30 kHz and the States method[2] was used for quadrature detection in the indirect dimension. Two experiments, each with 16 scans were acquired at each of the 24 t_1 increments. The recycle delay in these 2D experiments was 5 s.

Solid-state ^{13}C and ^{15}N CP-MAS NMR and 2D ^{15}N-^{15}N correlation experiments were carried out on a Bruker AVANCE 200 instrument with a 4.7 T magnetic field strength and operating at 200.5, 50.42, 20.32 MHz Larmor frequencies for ^{1}H, ^{13}C, and ^{15}N, respectively. The experiments were performed with a 7 mm double resonance CP-MAS probe. The ^{13}C and ^{15}N experiments were carried out at MAS frequencies of 7 and 4 kHz with cross-polarization contact times of 2 and 10 ms, respectively, employing recycle delays of 5 s and SPINAL-64 ^{1}H decoupling[3] with a ^{1}H nutation frequency of 46 kHz during the acquisition period. The ^{13}C and ^{15}N CP-MAS NMR spectra were acquired with 8000 and 64 scans, respectively. The 2D ^{15}N-^{15}N DQ correlation experiments were performed with the $SR26_4^{11}$ symmetry-based dipolar recoupling sequence[4] with 8 ms of DQ excitation and reconversion with a ^{15}N recoupling nutation frequency of 26 kHz and a ^{1}H cw decoupling nutation frequency of 77 kHz. The 2D ^{15}N-^{15}N refocused INADEQUATE experiment[5] was carried at a MAS frequency of 4 kHz MAS with a half-echo delay time of 10 ms. During the DQ excitation, evolution, and reconversion periods, ^{1}H SPINAL-64 decoupling was applied with a ^{1}H nutation frequency of 46 kHz. For both ^{15}N-^{15}N correlation experiments, the States method was used for quadrature detection in the indirect dimension and 64 t_1 increments, each with two experiments, were acquired. The dipolar $SR26_4^{11}$ spectra were acquired with 16 scans per experiment while the J-coupling INADEQUATE spectra were acquired with 128 scans per experiment.

^{1}H and ^{13}C chemical shifts were referenced to TMS using adamantane as a secondary reference by setting the ^{1}H signal to 1.85 ppm and the downfield ^{13}C signal to 38.48 ppm. ^{15}N chemical shifts were referenced to liquid ammonia using glycine as a secondary reference by setting the ^{15}N signal to 32.1 ppm. The shifts can be converted to the chemical shift scale referenced with respect to CH_3NO_2 by subtracting 379.5 ppm.

Peak Assignments



With a ^{15}N-enriched sample, it is straightforward to obtain ^{15}N NMR spectra of the G∧C sample. The five peaks arising from the five ^{15}N-labelled sites are clearly resolved. Based on the isotropic ^{15}N chemical shift,[6] the three upfield signals (76.4, 89.2, and 138.0 ppm) can be assigned to nitrogen sites with proton attached (proton donors) and the two most downfield peaks (167.3 and 176.1 ppm) are due to nitrogens without directly attached proton.[7]

The spinning sideband profiles in the ^{15}N CP-MAS spectra obtained at slow MAS frequencies (Figure S8) reveal the ^{15}N chemical shift tensors for each nitrogen (Table S2). In **1**, there are two nitrogens (at 176.1 and 167.3 ppm) with large chemical shift anisotropies. These peaks likely arise from the nitrogens that do not have directly attached protons. This result is consistent with the above observation that their isotropic chemical shifts resonate at relatively low field. In ^{15}N CP-MAS NMR spectra collected with a short CP contact time of 100 μs (not shown), these same peaks with the large chemical shift anisotropies are observed with very low signal intensity, providing a further indication that these peaks are the nitrogens without directly attached protons.

This is more clearly observed in the 2D ^{1}H-^{15}N correlation spectra (Figure 2C). Strong correlations are observed for the three nitrogens with directly attached protons, one of which (89.2 ppm) has correlations to two protons (7.8 and 8.9 ppm) and can thus be assigned to the NH_2 group (N16) and its attached protons can be assigned to H^c and H^d.

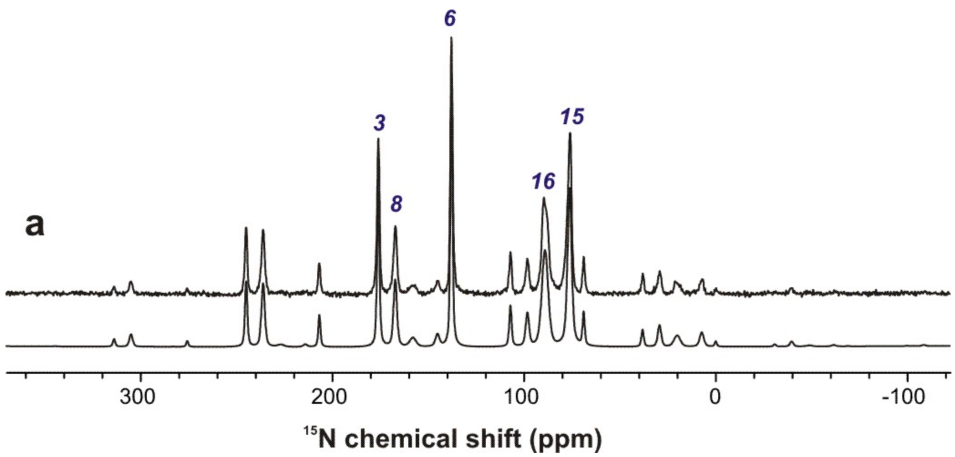


Figure S8. Experimental (*upper*) and calculated (*lower*) ^{15}N CP-MAS NMR spectra obtained at 4.7 T of (a) **1** at 1.4 kHz MAS frequency. The best-fit ^{15}N chemical shift tensors values are listed in Table S2. The isotropic peaks are labeled.

Based on their ^{1}H chemical shifts and the relative intensities, the methyl protons (H^e) can be assigned to the peak at 2.7 ppm. There is a weak correlation between the methyl protons and the upfield ^{15}N peaks at 76.4 ppm indicating that these can be assigned to N15 (the nitrogen to which the methyl group is attached). The strong ^{1}H-^{15}N correlations for N15 enables the assignment of the directly attached proton H^a to the peak at 9.2 ppm.

The strong ^{1}H-^{15}N correlations for N6 and H^b, together with the ^{15}N isotropic chemical shift and spinning sideband analysis, enable the assignment of N6 to 138.0 ppm and H^b to 13.7 ppm. The chemical shift value (13.7 ppm) of H^b indicates a NH•N hydrogen bond.[8]

Table S2. ^{15}N chemical shift tensors determined from spinning sideband profiles in slow CP-MAS spectra at 4.7 T.

Site	δ_{iso} (ppm)	δ_{aniso} (ppm)	η
N3	176.1	-136.9	0.44
N6	138.0	80.1	0.93
N8	167.3	-187.6	0.46
N15	76.4	70.9	0.57
N16	89.2	80.0	0.49

The isotropic value, anisotropy, and asymmetry parameters for the chemical shift interaction are related to the principal elements of the shift tensor according to $\delta_{iso} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$, $\delta_{aniso} = \delta_{zz} - \delta_{iso}$, $\eta = (\delta_{yy} - \delta_{xx})/\delta_{aniso}$ where the principal elements are labeled and ordered according to $|\delta_{zz} - \delta_{iso}| \geq |\delta_{xx} - \delta_{iso}| \geq |\delta_{yy} - \delta_{iso}|$.

The other nitrogens can be assigned from the 2D ^{15}N-^{15}N DQ correlation spectra (Figure 2D). As shown in Figure 2D, N16 at 89.2 ppm is correlated to only one other peak at 176.1 ppm. This peak can therefore be assigned to N3, the only nitrogen that is in close spatial proximity to N16. Consequently, the only unassigned signal at 167.3 ppm is due to N8. This assignment can further confirmed in the 2D ^{15}N-^{15}N spectrum (Figure 2D) by the observation of correlations of N8/N6 and N8/N15 due to their close spatial proximity to N8.

The group of peaks between 4 and 6 ppm in the ^{1}H spectrum (Figure 2B) belongs to the protons of the allyl group. Based on relative signal intensities, the peaks near 6 ppm are assigned to H^g, but there remains some ambiguity about the assignment of H^f and H^h. Based on isotropic chemical shifts, it is expected that H^h protons would be less shielded than the H^f protons due to the C=C double bond. Therefore the peaks near 5 ppm are assigned to H^h and the peaks near 4 ppm are assigned to H^f.

The peaks at 1 and 7 ppm marked w1 and w2 were assigned to bound water inside the RNT channel since there are no correlations with ^{15}N observed nor any ^{1}H-^{1}H correlations with any of the G∧C peaks. It should be noted that the peak for bulk-like water usually resonates at

4.8 ppm. The remarkable upfield/downfield shift observed indicates a considerable through-space shielding/deshielding effect of the RNTs on the confined water.[9-11] The fact that ^{1}H-^{1}H DQ correlation peaks are observed along the diagonal (Figure 2E) suggests that the interior water has a degree of rigidity (or restrained mobility), i.e, the water molecules lack the full (isotropic) mobility that would lead to averaging of the dipolar interactions to zero. The observed correlations are likely to be internal dipolar interactions (e.g. between protons of a single water molecule). This is consistent with the water molecules being located within the nanotubes in which their residual mobility is sufficient to weaken the dipolar couplings to the nuclei in the G∧C units that make up the walls of the RNT but not sufficient to fully average out the much stronger internal dipolar couplings.

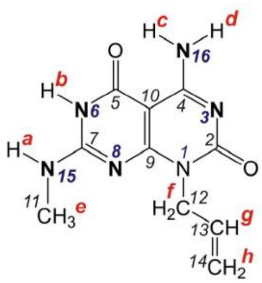


Table S3. Solid-state ^{1}H and ^{15}N isotropic chemical shifts and observed correlations for **1**.

Site	**^{1}H chemical shifts /ppm**	**Site**	**^{15}N chemical shifts /ppm**
H^a	9.2 (H^b, H^e) (N15)	N3	176.1 (N6,N16) (H^b)
H^b	13.7 (H^a, H^d) (N3, N6)	N6	138.0 (N3, N8, N15) (H^b)
H^c	7.7 (H^d) (N16)	N8	167.3 (N6, N15)
H^d	8.8 (H^b, H^c) (N16)	N15	76.4 (N6, N8) (H^a, H^e)
H^e	2.7 (H^a)	N16	89.2 (N3) (H^c, H^d)
H^f	4.4 (H^f, H^g)		
H^g	6.0 (H^f, H^h)		
H^h	5.0 (H^g, H^h)		

The sites listed in parentheses are those for which strong correlations are observed in 2D NMR experiments.

^{13}C NMR

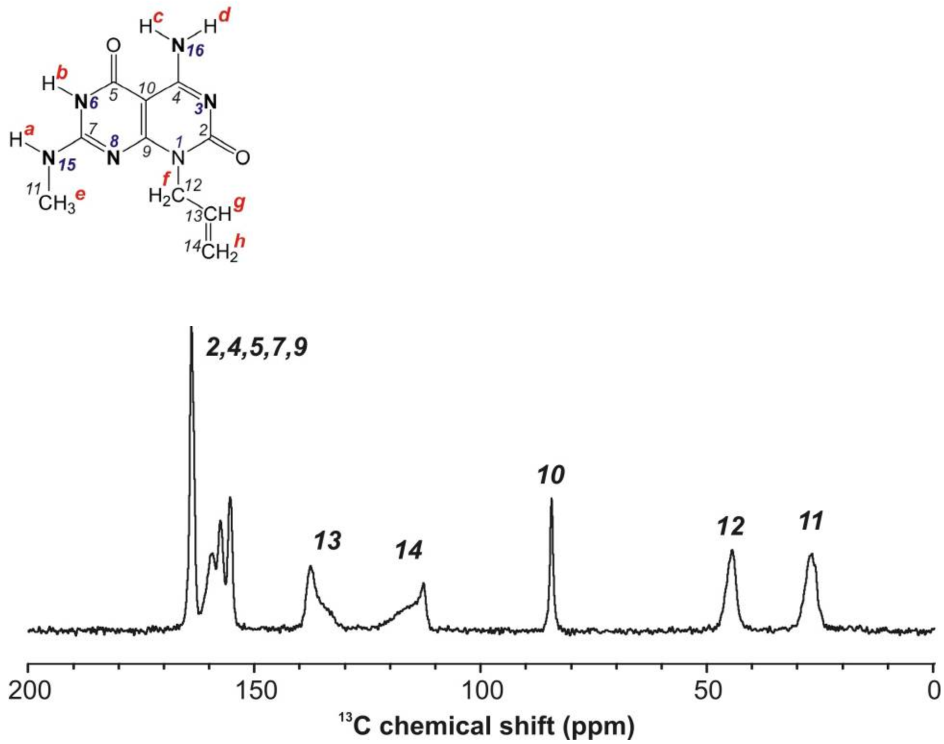


Figure S9. ^{13}C CP-MAS NMR spectrum of **1** obtained at 4.7 T. Wherever possible, the peaks were assigned based on similarities to the solution NMR spectrum.

X-ray Powder Diffraction. A solution of compound **1** (0.25 g/L in MeOH) was concentrated at room temperature under reduced pressure (rotovap). The samples were analyzed in transmission mode using a beam stopper on a Bruker D8 Discover equipped with Cu K_α source and Bruker HiStar GADDS detector.

Electron microscopy and atomic force microscopy

Sample preparation. A 0.25 g/L solution of **1** in methanol was drop-cast on a 600 mesh carbon coated copper grid, excess of solution was blotted, and the grid was dried in vacuum at rt. SEM (Figure S10) and TEM (Figure S11) revealed the presence of thick (~40 nm) nanotube bundles. A portion of 0.25 g/L solution was diluted down to 0.05 g/L in methanol and sonicated at 40°C.

Thinner RNT bundles and single nanotubes were obtained from the sonicated solution as imaged by SEM and AFM (Figures S12-S14).

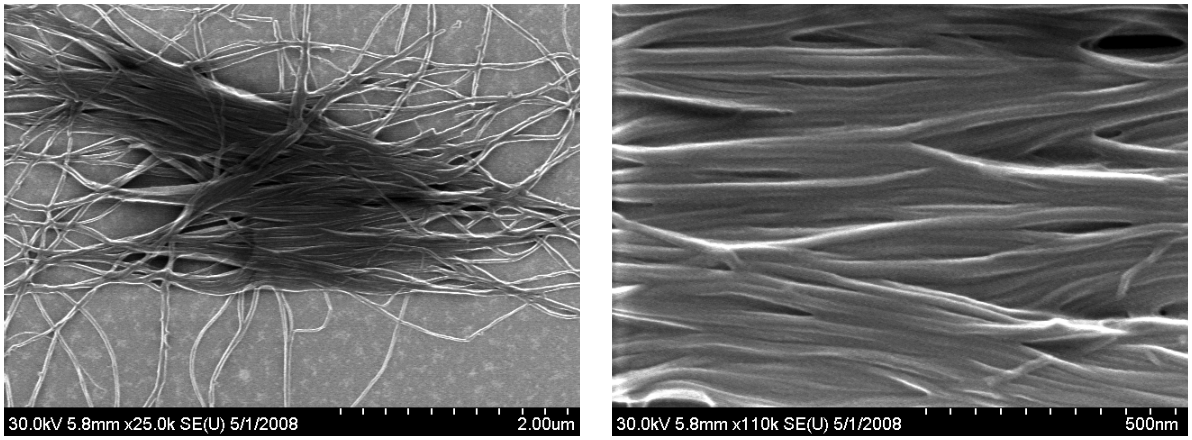


Figure S10. SEM images of 1 cast from methanol after 30 min of sonication in hot methanol (~0.05 g/L, carbon film).

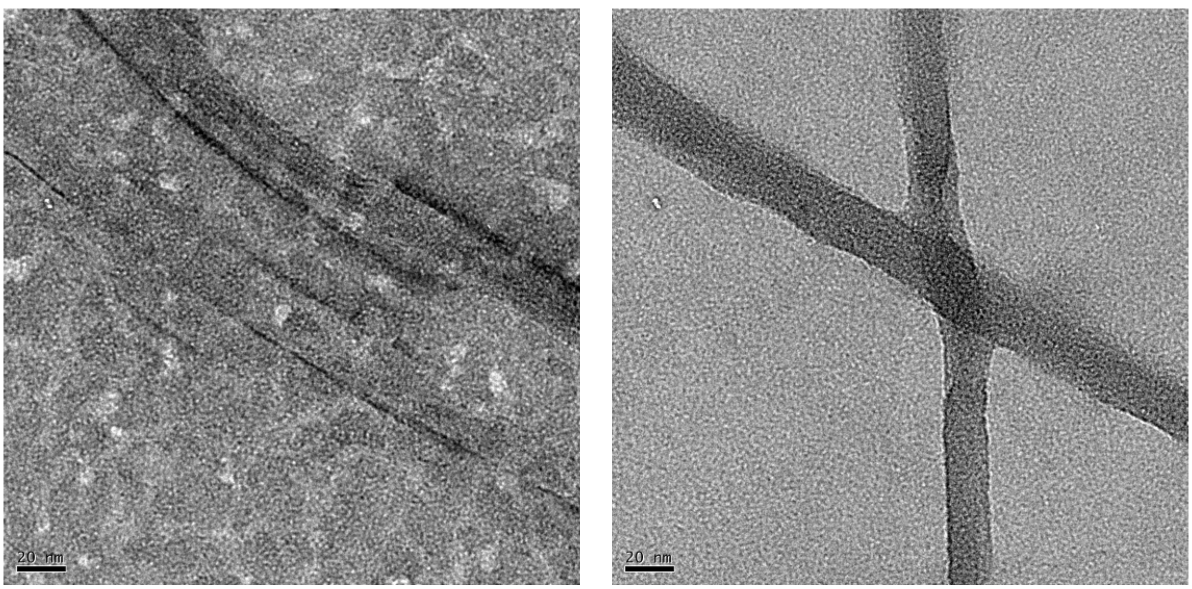


Figure S11. TEM images of RNTs assembled form **1** in methanol (*ca.* 0.05 g/L) and cast on carbon-coated TEM grids, unstained (left) and stained with uranyl acetate (right). The hydrophobic nature of the RNT surface prevents efficient staining and results in low contrast in TEM images. Average diameter measured for a single nanotube from the *ca.* 80 TEM measurements is 2.2 ± 0.3 nm.

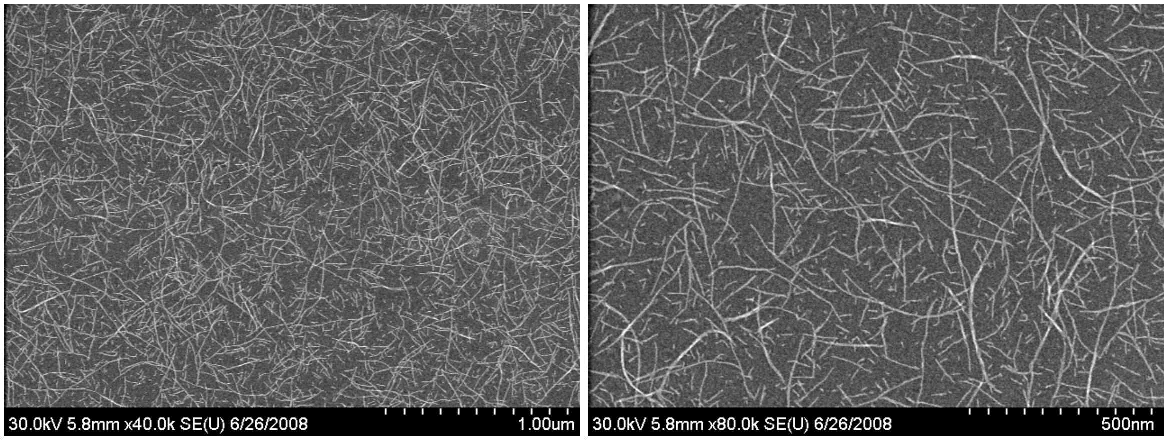


Figure S12. SEM images of RNTs assembled from **1** (*ca.* 0.05 g/L), cast carbon-coted TEM grid from methanol after 30 min of sonication in hot methanol.

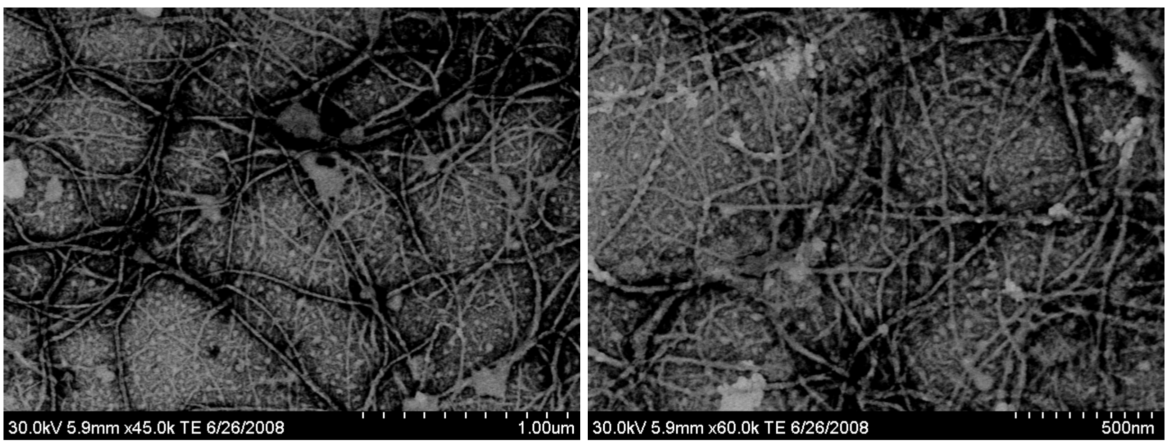


Figure S13. Transmission mode SEM images of RNTs assembled from **1** (*ca.* 0.05 g/L) on carbon-coated TEM grids after 30 min of sonication in hot methanol and staining with uranyl acetate.

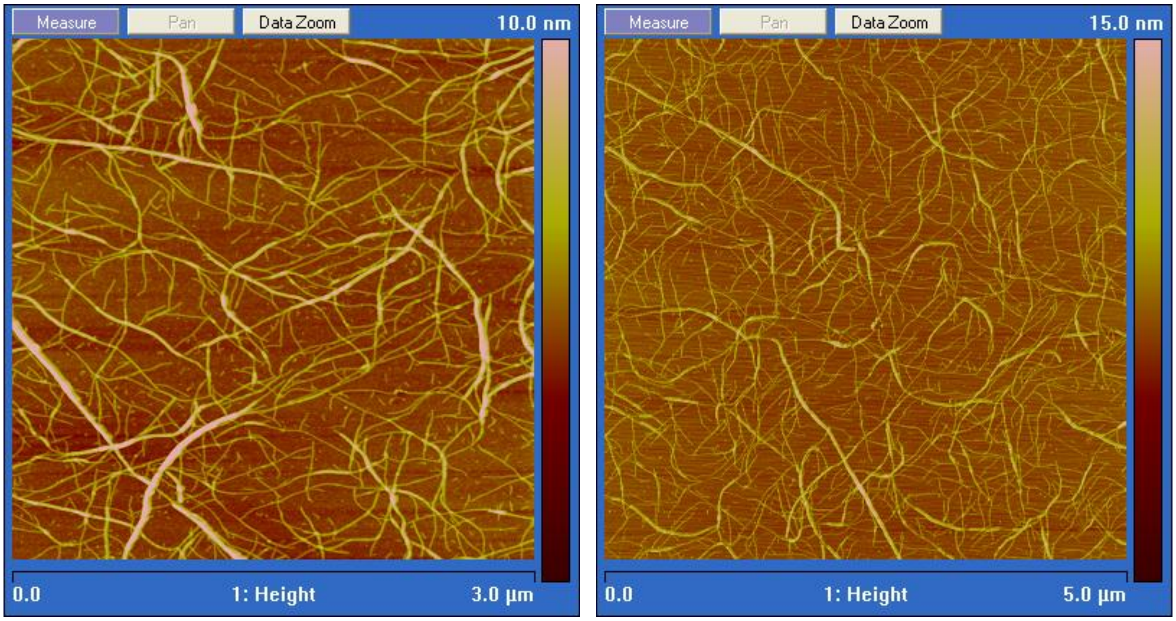


Figure S14. TM-AFM images of RNTs assembled in methanol from **1** (*ca.* 0.05 g/L, mica). Average single nanotube diameter measured from ca. 80 measurements is 2.0 ± 0.4 nm.

References

1. (a) Schnell, I.; Spiess, H. W. *J. Magn. Reson.* **2001,** 151, 153-227. (b) Feike, M.; Demco, D. E.; Graf, R.; Gottwald, J.; Hafner, S.; Spiess, H. W. *J. Magn. Reson. A* **1996**, *122*, 214-221. (c) Schnell, I. *Prog. Nucl. Magn. Reson. Spectr.* **2004**, *45*, 145-207
2. Sorensen, M. D.; Meissner, A.; Sorensen, O. W. *J. Biomol. Nucl. Magn. Reson.* **1997,** 10, 181-186
3. Hodgkinson, P. *Prog. Nucl. Magn. Reson. Spectr.* **2005,** 46, 197-222.
4. (a) Levitt, M. H. *J. Chem. Phys.* **2008,** *128*, 5. (b) Kristiansen, P. E.; Carravetta, M.; Lai, W. C.; Levitt, M. H. *Chem. Phys. Lett.* **2004**, *390*, 1. (c) Brouwer, D. H.; Kristiansen, P. E.; Fyfe, C. A.; Levitt, M. H. *J. Am. Chem. Soc.* **2005**, *127*, 542.
5. (a) Lesage, A.; Bardet, M.; Emsley, L. *J. Am. Chem. Soc.* **1999**, *121*, 10987; (b) Pham, T. N.; Masiero, S.; Gottarelli, G.; Brown, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 16018-16019.
6. Buchner, P.; Maurer, W.; Ruterjans, H. *J. Magn. Reson.* **1978**, 29, 45-63.

7. Pham, T. N.; Masiero, S.; Gottarelli, G.; Brown, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 16018-16019.

8. Webber, A. L.; Masiero, S.; Pieraccini, S.; Burley, J. C.; Tatton, A. S.; Iuga, D.; Pham, T.; Spada, G. P.; Brown, S. P. *J. Am. Chem. Soc.* **2011**, *133*, 19777-19795.

9. Chen, Q.; Herberg, J. L.; Mogilevsky, G.; Wang, H.; Stadermann, M.; Holt, J. K.; Wu, Y. *Nano Lett.* **2008**, *8*, 1902-1905.

10. Brunklaus, G.; Koch, A.; Sebastiani, D.; Spiess, H. W. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4545-4551.

11. Kurotobi K. Murata, Y. *Science***, 2011**, *133*, 613-616.